PRODUCTION OF HIGH TEMPERATURE GREASE USING SPENT BLEACHING EARTH (SBE)

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A thesis submitted in fulfillment of the requirement for the award of the degree of Bachelor of Chemical Engineering

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DECEMBER 2010

ABSTRACT

Nowadays, the disposal problem of Spent Bleaching Earth (SBE) from oil palm industry has become a serious environmental issue. Therefore, attempt was made in this research to utilize the SBE as raw material in the production of high temperature grease. The scope of this research includes preparation of calcium fluoride as thermal resistance additives, grease preparation and analysis on the grease produced. The parameters studied for grease preparation are effect of different ratio of SBE and fumed silica as thickener and effect of mixing time. The ratios of SBE used in grease formulation were varied from 100 wt. % to 60 wt. % of thickener weight. The best ratio chosen from grease formulation is based on the dropping point test before it was further used for second parameter. As a second parameter, the mixing time of grease preparation was varied at 1, 2, 3, 4 and 5 hours. The grease produced was analyzed for dropping point, worked penetration, copper corrosion, organic content using FTIR and metal content using AAS. The results obtained were compared to the National Lubricating Grease Institute (NLGI) Guide to classify the grease. Results indicate that the best ratio for grease formulation is 90% of SBE and 10% of fumed silica. Therefore, the usage of fumed silica which is very expensive can be reduced. Results also shows that the consistency of grease decreased as the mixing time increased. With refer to NLGI standard, the consistency of all grease at mixing time 1 to 5 hour is in the range of 2 to 4 grade number and can be classified as high temperature grease since its dropping point is higher than 260^{o}C. As a conclusion, the findings from this research has the high potential to help in solving the environmental problem on SBE disposal which is in line with the government campaign to reduce waste in daily life and indirectly can reduce the production cost with this SBE based grease.

ABSTRAK

Pada masa ini, masalah pembuangan tanah liat pemutih terpakai (SBE) dari industri kelapa sawit menjadi isu alam sekitar yang serius. Oleh kerana itu, usaha dilakukan dalam kajian ini untuk menggunakan SBE sebagai bahan mentah dalam penghasilan gris bersuhu tinggi. Kajian ini merangkumi penyediaan kalsium fluorida sebagai penambah tahan panas, penghasilan gris dan analisis terhadap gris yang dihasilkan. Pembolehubah yang dikaji ialah kesan daripada perbezaan nisbah SBE dan silika kesal sebagai pemekat dan kesan masa campuran. Nisbah SBE digunakan dalam formulasi gris berbeza-beza dari 100 *wt.* % hingga 60 *wt.* % daripada jumlah berat pemekat. Nisbah terbaik dipilih daripada formulasi gris berdasarkan pada ujian titik pertukaran menjadi cecair sebelum nisbah itu diguna pakai untuk pembolehubah kedua. Untuk pembolehubah kedua, terdapat lima waktu pencampuran yang berbeza ketika penghasilan gris telah dikaji iaitu pada 1, 2, 3, 4 dan 5 jam. Gris yang dihasilkan telah menjalani ujian titik pertukaran menjadi cecair, ujian penembusan, ujian hakisan ke atas kuprum, ujian kandungan organik menggunakan FTIR dan ujian kandungan besi menggunakan AAS. Keputusan yang diperolehi dibandingkan dengan panduan daripada *National Lubricating Grease Institute* (NLGI) untuk menetapkan kelas gris. Keputusan kajian menunjukkan bahawa nisbah terbaik untuk perumusan gris adalah 90% SBE dan 10% kesal silika. Oleh itu, penggunaan silika kesal yang sangat mahal dapat dikurangkan. Selain itu, konsistensi gris menurun dengan peningkatan masa pencampuran. Merujuk kepada panduan NLGI, konsistensi gris adalah dalam julat nombor 2 hingga 4 dan boleh digolongkan sebagai gris pada suhu tinggi apabila titik pertukaran menjadi cecair lebih tinggi daripada 260^{o}C. Sebagai kesimpulan, penemuan daripada kajian ini berpotensi tinggi untuk membantu dalam menyelesaikan masalah persekitaran iaitu pembuangan SBE dan ini selaras dengan kempen kerajaan untuk mengurangkan sisa dalam kehidupan seharian, secara tidak langsung dapat mengurangkan kos penghasilan gris dengan terhasilnya formulasi gris daripada SBE.

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LIST OF ABBREVIATIONS

AAS	-	Atomic Absorption Spectroscopy
ASTM	-	American Standard Testing Materials
AW	-	Anti- wear
EP	-	Extreme Pressure
FTIR	-	Fourier Transform Infrared
MDF	-	Medium Density Fibreboard
NLGI	-	National Lubricating Grease Institute
SBE	-	Spent Bleaching Earth

LIST OF SYMBOLS

^{o}C	-	Degree Celcius
”	-	Inch
%	-	Percentage
wt. %	-	Weight percentage
ppm	-	part per million

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Grease is a semi-solid lubricant possessing higher viscosity than oil formed by three composition which are base fluid (60-95%), thickener (5-25%) and additives (0-10%) (Adhvaryu *et al.,* 2005). The function of base fluid is giving the lubricating properties to the grease itself. Mineral oil, synthetic oil and vegetable oil are usually used as grease base fluid to substitute the animal fat that use in yesteryears. Thickener on the other hand is used to thicken the grease and hold the matrix together to avoid mobilizes of grease structure. It is also function as a gelling agent. Basically, fatty acids soap of alkali metals is used as a thickener such as lithium soap, sodium soap and calcium soap or inorganic thickeners, such as bentone or silica are considered are to be not harmful to the environment (Kragujevac *et al.*, 2005). Additives can be classified regarding different aspects to enhance the grease properties base on their applications. Antioxidant, antifoam, antiwear, extreme pressure and high temperature agent are usually used as an additive in grease production. Base fluid generally cannot satisfy the requirements of high performance grease without using the advantage of additives.

High temperature grease and oil is often a synthetic lubricant as the temperature range of conventional grease and oils is easily exceeded by the demands of modern machinery and equipment. Plastic extrusion machinery, glass manufacture, chipboard and MDF plants all need high temperature grease and oil. As the marketing requirement of high temperature grease is increasing and widely used, other method to produce grease should be explored.

Spent bleaching earth (SBE) is a solid waste material generated from the bleaching process of oils and fats. It is generated from pre-treatment of crude palm-oil in refinery in which involves degumming and bleaching. SBE is recycled using solvent extraction process to remove residual oil before reactivation by heat treatment. Regenerated SBE still has adsorptive capabilities and can be reused in the bleaching of crude palm oil.

The disposal of by-products, spent material and industrial waste is one of the major problems face by oils industry today. Regulations for disposal are become stricter. The disposal method must be carefully chosen according to special regulation as directed by environmental department. In Europe, oil and fat industry as well as their by-product and spent material received huge concerned and special enforcement on reuse and regeneration as much as possible for chemical or technical purposes are made (Svensson, 1976).

Malaysia, as the second largest oil palm producer in the world generate large amount of SBE. So, everyday there are a large amount of SBE released from the industry as waste based on worldwide oil production. SBE is commonly disposed at landfills nowadays. However, disposal of untreated spent bleaching earth from crude palm oil industry into landfill is increasingly unacceptable because it is s hazardous to environment due to the substantial oil content in the earth. The SBE has a strong odor, and spontaneous ignition easily occurs if contact with air.

Therefore, a new formula of producing grease should be investigated to solve these two main problems. In that case SBE from oil palm industrial waste respectively will play an important role as a continuous source of raw material for grease production.

1.2 Problem Statements

It is estimated that about, 600000 metric tons or more of bleaching earth are utilized worldwide in the refining process based on the worldwide production of more than 60 million tones of oils (Kheang *et al*., 2006). The similarity of physical properties of regenerated SBE compared to the fresh clay opens for more applications as industrial adsorbents. Pollards *et al.* (1990) reported that SBE was effective in the stabilization or solidification of mixed streams organic matters.

In the oil refining industry, SBE served as by-product and it is containing high percentage of oil. Typically, SBE from oil palm industries contains 17-35% residual oil, metallic purities, fatty acids and gum. The SBE or this solid waste clay is disposed directly to the landfills without treatment causing severe water and air pollution problems (Fletto *et al.,* 2002). However, the dumping of spent clay directly in landfills and public disposal site has been prohibited in most country nowadays. The waste management concerning about the disposal of residues from refineries industry.

Recovery of oil and the reuse of spent bleaching clay are the areas where great opportunity exists for cost saving in the oil processing industry (Fletto *et al.,* 2002). Besides that, the characteristics and lubrication properties of the residual oil and composition of the resulting methyl esters during bleaching shows that the oil has good lubricity such as suitable viscosity range and high viscosity index for use as a lubricant base. SBE can also be used as raw material for high performance grease so that it can maintain a thin film over the metal parts of machines and the oil contact surface to smoothen and lubricate them. Therefore, an economic alternative to solve the disposal problem and current treatment of SBE is by re-used the SBE to produce other oil product such as high temperature grease.

1.3 Research Objective

The objective of this research is to study the production of high temperature grease using spent bleaching earth (SBE).

1.4 Research Scopes

In order to achieve the objective as stated above, the following scopes of study have been identified:

i. To produce a thermal resistant additive which is Calcium Fluoride (CaF_2) for grease formulation.
ii. To study the effect of different ratio of SBE and fume silica on grease formulation using additive produced from 1.4 (i).
iii. To study the effect of different mixing time on grease formulation at constant ratio from 1.4 (ii).
iv. To characterize the grease produced by dropping point, work penetration, copper strip, AAS and FTIR test.
v. To compare the characteristics of grease produced.

1.5 Rationale and Significance

It is a responsibility as a nation and society to become more concern in handling a large amount of waste generated by industry every day. Waste to wealth is a good approach in order to promote zero waste concepts. As highlighted in the previous section, disposal of SBE has become an environmental issue since the high content of oil in SBE can cause pyrogenic effect. Although attempts have been made by other researcher to recover the oil contains in the SBE, it still does not resolve the main problem which is the disposal of SBE.

Besides that the increasing price of mineral oil due to the high market requirement of petroleum product but with limited mineral sources also becomes an important reason to conduct this research. Utilizing SBE as raw material to produce high temperature grease indirectly saves a lot of money due to conversion of waste into wealth. It is hoped that by utilizing SBE as one of the raw material in grease formulation will able to solve the disposal problem and at the same time reduce grease market price.

CHAPTER 2

LITERATURE REVIEW

2.1 Background of Grease

Lubricating grease is a semisolid product which is generally highly structured colloidal dispersions, consisting of a thickener dispersed in synthetic or mineral oil. Grease is the preferred form of lubrication in hard-to-reach places in a mechanically rubbing or dynamic systems. Lubricating greases has been a need during the ancient times. The Greeks and Roman used animal fat and also vegetable oil as lubrication. They used the animal fat to run machines of various kinds, mills, pulleys, windlasses, chariots and fast carriages. Nowadays, with the modern and advanced technology, the animal fats are not in use as lubricants (Harris *et al.*, 1974).

Grease acts as reservoir for lubricant-based fluids and additive molecules (Adhvaryu *et al.*, 2005) and most of its functional properties depends on their ability to flow under force, shear stability, resistant toward viscosity changes with temperature and pressure, water stable, seal out contaminants, decrease dripping and spattering. The dependability of lubricating grease depends on their physical properties that are most related to the grease structure, which is obtained by the proper selection of ingredients and processing. Additives are usually introduced during the cooling phase of grease making and they remain dispersed in the matrix.

These additives are found to enhance some of the functional properties of the base oil in the grease to achieve high performance requirement such as oxidation, load-bearing, anti-wear, anti-corrosion, and anti-rust. A typical composition of grease as illustrated in Figure 2.1 includes base fluids, thickener, and additives. The base fluid is contained and stabilized in the matrix by the fiber structure of the soap molecules. Metals usually used in the soap composition include lithium, calcium, sodium, aluminum, and titanium as grease thickener (Adhvaryu *et al.*, 2005).

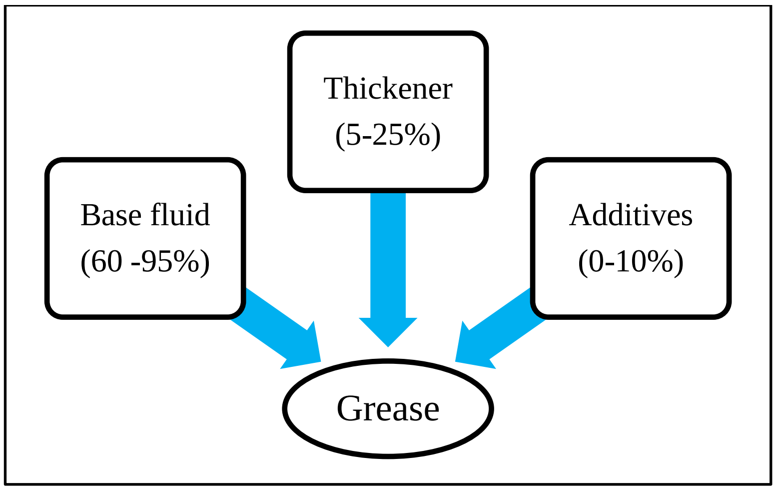

Figure 2.1: Typical composition of grease

Greases fail more rapidly as temperature of operation increases. The most obvious reason for failure lies in the melting point of the thickener or dropping point of the grease. The latter involves a complex of melting and bleed. Evaporation may be significant at high temperatures. Oxidation also increases rapidly as temperature rises. Most mineral-oil-based greases (of adequate dropping point) will operate successfully to about 250 °F (121°C). A smaller number can handle 300 °F (149°C). A few mineral-oil-based greases can operate to about 350°F (177 °C). Around this temperature, synthetic fluids are preferred or required. As service temperature rises, frequency of lubricant addition and relubrication must increase (NLGI, Lubricating Grease Guide, 2006).

The thickening agent commonly used is a metallic soap prepared by saponification of a fatty substance, but can be also a non-soap based such as polyurea or organoclay. The organoclay is widely used in various applications in industry as structure-forming and thickening agents in inks, paints, cosmetics, drilling fluids and lubricating grease formulations due to the ability of swelling and gel formation on organic media cause. Besides that, the use of organoclays as thickening agents in grease formulations confers excellent thermal stability and high performance qualities to the greases (Chtourou *et al.*, 2006). The dispersion of organoclays in lubricating oil is described as the mechanism which separates the individual agglomerated organoclay particles. Dispersion is typically accomplished by the use of polar activators (alcohols, ketones, amides, nitriles) and mechanical shear. The gel structure of the grease is caused by hydrogen bonding between dispersed organoclay particles creating a gel network.

2.1.1 Advantages and Disadvantages of Grease

Grease has their own advantages that make them more suitable to use as lubricant compared to other oil. Some of the reasons are grease has the ability to stay in place or immobilize and does not readily leak from the bearing because it incorporates the use of a thickener matrix. Besides that, it also can seal out the contaminants that can reduce the efficient of the lubricant. Grease also decreases dripping, splattering and leakage due to its high consistency. As its function is to reduce friction, grease can reduce the noise of machine during operation so that the machinery also tends to need less power while operating. In addition, because of its composition which have base oil, thickener and additive which is have their own properties to enhance the grease performance, it can make the greases can work under extreme operating conditions (*MOBIL* Grease).

However, greases may bear some advantages such as it may not reach all places in need of lubrication because it has high viscosity. Besides that, greases do not work as cooling agent because it cannot dissipate heat by convection like circulating oil due to its consistency. Another disadvantage is grease cannot be used at as high speeds as liquids because grease has more resistance to motion at start-up than oil (*MOBIL* Grease).

2.2 Production of Grease

In 1400, animal fat such as mutton or beef fat was sometimes used as grease by mixed the fats with lime to reduce the friction in chariot wheels. With a right condition, lime and oil will be heated to produce grease. However, modern greases were not commercially available until more than 3 300 years later. The first grease produced was a calcium soap grease then it followed by lithium, barium and calcium complex greases which are introduced in 1930s and 1940s. Aluminum complex greases followed in the early 1950s, but modern lithium complex greases did not enter the market until the early 1960s (NLGI Lubricating Grease Guide, 2006).

The grease production data has been collected from manufacturers by the National Lubricating Grease Institute (NLGI) since the early 1960s. The trends can be noted by reviewing the historical data as illustrated in Figure 2.2.

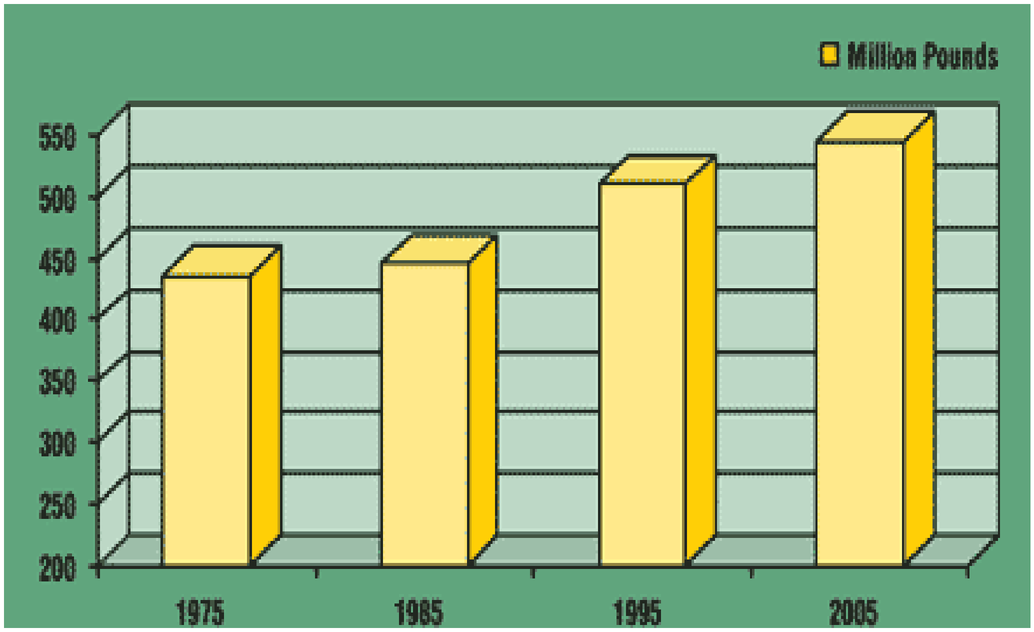

Figure 2.2: Grease production from 1975 till 2005 (NLGI Lubricating Grease Guide, Fifth Edition, 2006)

There are two types of process route in grease manufacturing which is batch process or in-line process. Details descriptions are provided in Section 2.2.1 and 2.2.2.

2.2.1 Batch Process

For batch process, typical grease kettle with capacity ranged from 2 tons (4000 lbs) to 20 tons (40,000 lbs) is used. This grease kettle are heated with steam or hot oil to temperature approximately at 200°C (395 °F) or higher. In order to improve mixing efficiency, rotating paddle which can force the grease in appropriate directions is installed in the kettle. Besides that, kettles also have recirculation pumps to provide additional vertical mixing action and to transfer the grease to other processing equipment such as a homogenizer. Homogenizer is used to ensure the grease is homogenized mixed by means of milling. It has own purposes such as enables the grease to withstand a shearing action therefore only little changes in consistency during service (Jones, 1968).

2.2.2 In-Line Process

In-line process is differing from batch process because it is a continuous process. The process is begins with saponification followed by dehydration before finishing stage. This process is more flexible, fast and has a better process control. Figure 2.3 shows a comparison between batch and in-line grease manufacturing process. Detail explanations on the stage involve during grease manufacturing process is provided in Section 2.2.3.

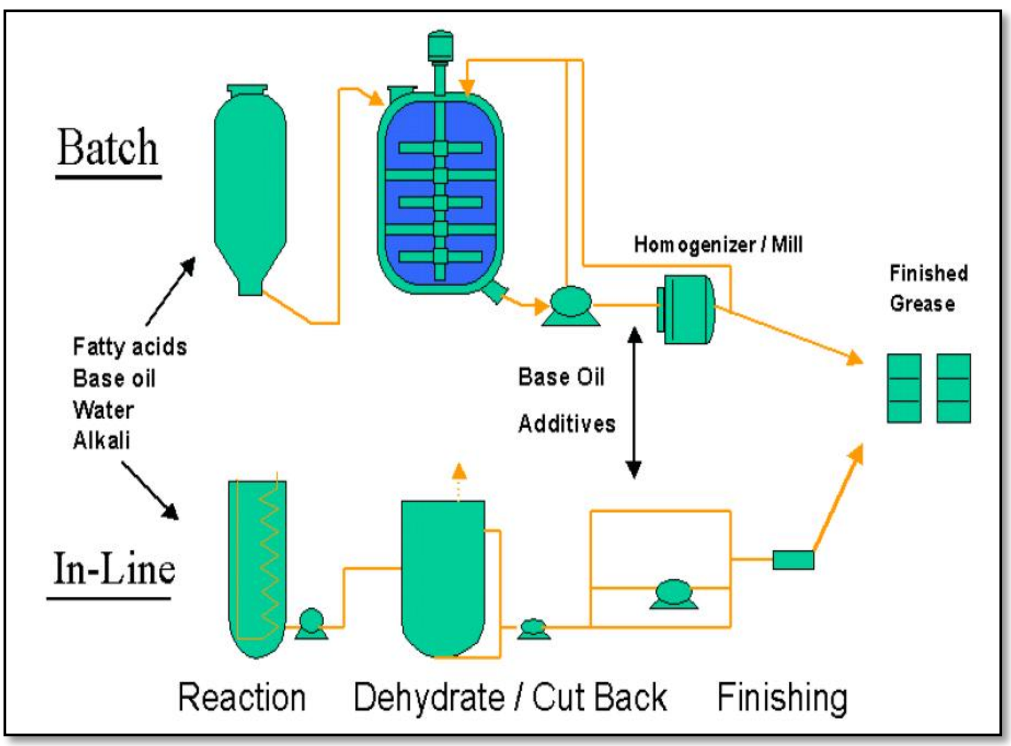

Figure 2.3: Comparison of grease manufacturing process

2.2.3 Stages in Grease Manufacturing

2.2.3.1 Manufacturing of Soap-Based Grease

The production or manufacturing of soap base grease can be divided into four stages. The stages include saponification, forming a solution, soap recrystallization and grease finishing (Jones, 1968). The detail explains are provided following section.

2.2.3.1.1 Saponification

Saponification can be defined as a process when a fatty acid reacts with an alkali and the salt produced is called soap. Most animal and vegetable fats contain glycerin which combined with fatty acids. During saponification process, fat is separated into fatty acids and glycerin by reacting with the alkali. Then, the fatty acid reacts with the alkali to produce soap and water. The reaction carried out in the reaction vessel because it operates at high temperature and needs heat in order to run a quick reaction and water also added in many cases.

There are many types of fats and fatty acids used in grease manufacturing. The cheaper greases usually made up from calcium hydroxide as the alkali and fats such as tallow, bone grease and whale oil products (Jones, 1968c). As time move on, the formulation of grease always improve in order to produce grease with a good quality. Therefore, it is quite common to find specific fats that can be used to enhance grease properties. When the fats with higher concentration are used as raw materials, it is obviously possible to maintain higher standard of product quality and manufacturing control. The soap produced from different alkali will imparts different grease characteristics.

2.2.3.1.2 Forming a Solution

The soap is transfer from reaction vessel into open kettle for structure forming and further cooling stage. Then, it will be continued heating until it dissolved in lubricant. During this process, dehydration may take place. In the previous section, water and glycerin are produced during saponification stage. Some glycerin may be lost during dehydration, but the rest will act as a structure modifier in the finishing stage and it will confer the resistance of heat stability to the grease. Its acts as a modifier of structure and can help grease some measure of heat stability. In order to achieve best result, heat is supply continuously until temperature reaches 250°C (Jones, 1968).

2.2.3.1.3 Soap Recrystallization

This stage is for cooling the soap that already obtained so that the structure is imparted to the grease. In order to produce satisfactory grease, the soap must have a good structure. If the structure is not suitable enough, the hardness of grease will reduces when subjected to a shearing action and the separation of oil or ‘bleed oil’ from grease may occur during storage until it becomes liquefied. The soap will dissolve in hot oil and it is cooled. Before reach ambient temperature the soap will therefore have recrystallized in various forms. Some of these forms take the shape of thick fibres and others short thin fibres when viewed under the electron microscope. The various structure of grease can be produced by controlling the cooling rate during recrystallization (Jones, 1968).

2.2.3.1.4 Finishing

As the last stage of production of grease, it is important to homogenize the grease by milling. At the end of this stage, the required of grease structure that has been formed will achieved except for non-soap thickened product. Milling has several purposes such as can enable the grease to withstand a shearing action and it is carried out by passing the grease through a gap between two surfaces (Jones, 1968). After milling process, it is necessary to filter the grease to remove any impurities or large particles of undispersed soap before final packaging.

2.2.3.2 Manufacturing of Non-soap Based Grease

The preparation of non-soap grease is often a relatively simple process compared to soap thickened grease. In a kettle with agitator, the thickener is gradually added to the base fluid or lubricant so that thickener will disperses in the lubricant by an efficient means of stirring and heating. According to Jones, 1968, the grease is wetted by means of wetting agent such as acetone that possessing polar chemical structure during the preparation of organiclay bentonite grease.